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A method of detecting the rare isotopes ^{85}Kr and ^{81}Kr by means of collinear laser photoionization of atoms in an accelerated beam

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Abstract. A method is suggested for detecting rare krypton isotopes, based on the collinear laser photoionization of atoms in an accelerated beam at the exit from a mass separator. The results of investigations into the two-step collinear laser photoionization of metastable krypton atoms in an accelerated beam are presented.

1. Introduction

The idea of creating a laser detector for rare long-lived isotopes (Letokhov and Mishin 1979, Letokhov 1980, 1981) has recently attracted widespread attention (Letokhov 1987, Lucatorto and Parks 1988). The following methods were suggested for the purpose: multiple-step resonance ionization (Letokhov and Mishin 1979), fluorescence burst technique (Balykin *et al* 1980, Keller *et al* 1981), multiple-step resonance ionization in a fast atomic beam (Kudryavtsev and Letokhov 1982), selective cooling of atoms (Balykin *et al* 1984), selective deflection of atoms (Cannon and Whitaker 1985), and isotope-selective depletion of excited states (Makarov 1982, 1983).

Radioactive noble gas isotopes, including ^{81}Kr and ^{85}Kr, are among the most interesting candidates for such a detection. The isotope ^{81}Kr is formed in the upper atmosphere under the effect of cosmic rays and has a half-life of 210 thousand years. Its relative abundance in the atmosphere is 5×10^{-13}. The detection of this isotope in ground water allows one to study its age and mixing rates, as well as other hydrological and geological processes occurring on the timescale of hundreds of thousands of years (Lehmann and Loosli 1988). The isotope ^{85}Kr, whose half-life is 10.8 years, owes its origin to nuclear reactors. At present, its relative abundance in the atmosphere comes to 5×10^{-11}. To detect this isotope is important both in monitoring environmental pollution (Weiss *et al* 1986) and studying the hydrological and geological processes accompanied by the intrusion of the atmospheric ^{85}Kr into the Earth's crust (Lehmann and Loosli 1988).

It is impossible to use tandem accelerators to detect krypton isotopes, for krypton forms no negative ions. Considerable progress has recently been made in the detection of krypton isotopes by means of laser resonance photoionization (Thonnard *et al* 1987). In these experiments, high isotopic selectivity was achieved in several stages of quadrupole and time-of-flight mass separation. The laser resonance photoionization process was Z selective, i.e., it allowed single krypton atoms to be detected without any isotopic selectivity by suppressing the isobaric background due to other elements.

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In this work, we present the results of our studies in the collinear laser photoionization of metastable krypton atoms in an accelerated beam. Based on these results, we suggest a method for detecting rare krypton isotopes and discuss its potential capabilities.

The essence of collinear laser photoionization of rare isotopes (Kudryavtsev and Letokhov 1982) is that the selective laser excitation of isotopic atoms to Rydberg states, followed by their electric-field ionization, is effected in a fast atomic beam produced by ion–atom charge exchange from an ion beam accelerated through a specified potential difference of U_A. The absorption spectrum of such a beam subject to collinear excitation features a large kinematic isotope shift in any atomic transition of any element. What is more, the Doppler absorption linewidth is additionally reduced by a factor of $2(eU_A/kT)^{1/2}$ as a result of velocity bunching (Anton *et al* 1978, Kaufman 1976). This allows for an extremely high excitation selectivity of the rare isotope atoms of interest.

Experiments on the detection of ^{3}He (Kudryavtsev *et al* 1988, Kudryavtsev and Petrunin 1988) showed the capability of this method to be limited by the background noise signal due to the accelerated atoms in the beam colliding with the residual gas molecules. In the case of helium, the noise signal at a residual gas pressure in the system of 10^{-7} mmHg was equal to the photoion signal corresponding to a relative ^{3}He abundance of 10^{-6}. The background noise level was further reduced by a factor of 10^4 through time-of-flight isotope separation (Kudryavtsev *et al* 1989), which made it possible to detect ^{3}He at a relative abundance of 10^{-9} (Aseyev *et al* 1990).

2. Experimental set-up

Figure 1 shows a schematic diagram of the experimental set-up used to study the collinear laser photoionization of krypton atoms. A beam of Kr ions accelerated to an energy of $eU_A = 3$ keV was produced by means of a hot-cathode gas-discharge ion source and then focused with a single electrostatic lens and deflected by the deflector d_1. Such a deflection made it possible to do away with the neutral ion beam component and, in addition, to enter, by means of the mirror M, laser radiation to follow the ion beam. The beam thence entered a charge-exchange cell containing potassium vapour at a temperature 160 °C, and around one half of the ions exchanged their charge in a quasiresonant fashion with potassium atoms and turned into neutral atoms, a substantial proportion of them in the $1s_5$ ($5s[\frac{3}{2}]_2^o$) and $1s_3$ ($5s'[\frac{1}{2}]_0^o$) metastable states. The kinetic energy of the krypton atoms thus produced was equal to $e(U_A - U_R)$, where U_R is the

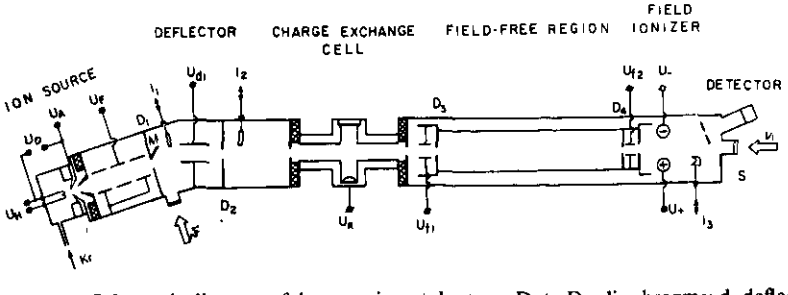

Figure 1. Schematic diagram of the experimental set-up: D_1 to D_4, diaphragms; d_1 deflecting capacitor; f_1 and f_2, filtering capacitors; I_1 to I_3, beam current meters; M, mirror; S, adjustable slit.

potential of the charge-exchange cell. The krypton ions that failed to exchange their charge were extracted from the beam by means of the filtering capacitor f_1, and the beam then entered a 1 m long field-free region where the metastable krypton atoms underwent a two-step laser excitation to Rydberg states. The exciting laser beam entered into the field-free region either strictly against the accelerated atomic beam (through the diaphragm D_4) or strictly with the beam (via the mirror M and the diaphragms D_2 and D_3). The Rydberg atoms leaving the field-free region were ionized by the electric field set up by two cylinders at potentials of U_+ and U_- and deflected by the same field onto a secondary electron multiplier through the adjustable slit S. Such a cross-field ionization scheme featured a dispersion due to the principal quantum number n, the Rydberg atoms differing in n being ionized at different field strengths and hence deflected through different angles (Kudryavtsev and Petrunin 1988).

The signal proportional to the charge on the secondary electron multiplier after each laser pulse was processed and averaged by means of a boxcar integrator and fed to an *XY* recorder. Weak signals were detected by means of a gated single-pulse counting system supplied by the secondary electron multiplier.

The flow of neutral Kr atoms at the exit of the set-up, I_3, was measured with a secondary emission transducer to be $10^{11}\ s^{-1}$.

The two-step excitation schemes used to raise the Kr atoms in the $1s_5$ ($5s[\frac{3}{2}]^o_2$) and $1s_3$ ($5s'[\frac{1}{2}]^o_0$) states to Rydberg states are illustrated in figure 2. The exciting laser radiation was generated by dye lasers pumped by a XeCl laser. The two exciting laser beams were brought together by means of a dielectric mirror and directed counter to the accelerated atomic beam. The dye laser bandwidths $\Delta\nu_{1,2}$ were around $1\ cm^{-1}$, which was much greater than the isotope shift ($0.03\ cm^{-1}$) in the absorption spectrum of the atomic beam and thus prevented isotope-selective laser excitation. The dye laser pulse energy ($Q_{\nu_{1,2}} = 3\ \mu J$) was only high enough to saturate the atomic transitions at

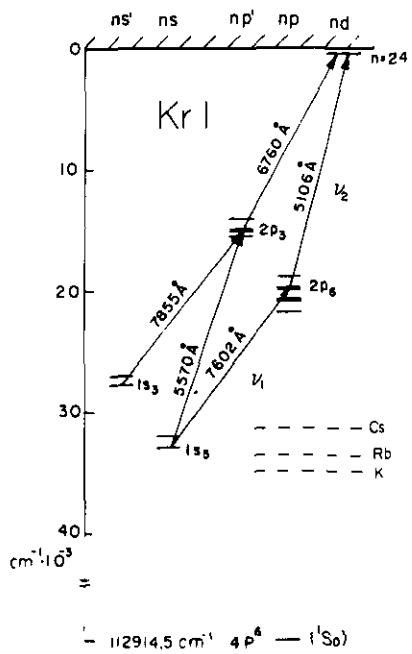

Figure 2. Energy level diagram and two-step laser excitation schemes for the Kr atom.

the first laser excitation step. The duration of the dye laser pulses was some 6 ns, and the delay time between the first- and second-step excitation pulses in the field-free region was around 4 ns. The pulse repetition frequency was 25 Hz.

The experiments on measuring the efficiency of laser photoionization and implementing the isotope-selective photoionization of Kr atoms via the intermediate level $2p_6$ ($5p[\frac{3}{2}]_2$) used the green line (5106 Å) of a copper-vapour laser at the second excitation step and a dye laser ($\Delta\nu_1 \simeq 1\ \mathrm{cm}^{-1}$) pumped by the yellow line (5782 Å) of the copper-vapour laser at the first step, the atomic transitions at both steps being fully saturated ($Q_{\nu_1} = 2\ \mu J$, $Q_{\nu_2} = 0.3$ mJ). The dye laser radiation was entered against the accelerated atomic beam and the green-line radiation of the copper-vapour laser with the beam. The repetition frequency of the laser pulses was 8.6 kHz, their duration equalled 15 ns, and the delay time between the first- and second-step excitation pulses in the field-free region ranged between 6 and 12 ns.

3. Photoionization schemes. Rydberg state spectrum

It was of interest to compare between the photoion signals obtained when exciting Kr atoms from the $1s_5$ ($5s[\frac{3}{2}]_2^o$) and the $1s_3$ ($5s'[\frac{1}{2}]_0^o$) states via one and the same intermediate state $2p_3$ ($5p'[\frac{1}{2}]_1$). In that case, the excitation conditions at the second step ($\lambda_2 = 6760$ Å) and the flow of neutral atoms through the system were maintained unchanged, and the atomic transitions at the first excitation step ($\lambda_1 = 5570$ Å; 7855 Å) were kept saturated. The photoion signal in the case of excitation from the $1s_5$ state was 2.9 ± 0.5 times that for excitation from the $1s_3$ state. Assuming that the metastable states get populated upon charge exchange in proportion to their statistical weights (5:1), the photoion signals in the case of excitation with a linearly polarized light should have been in the ratio 3:1 ($1s_5$ states with $|M_J| = 2$ cannot be raised using such a light to the $2p_3$ level ($J = 1$)).

Figure 3 shows the spectrum of Rydberg states in Kr, obtained by varying the second-step laser frequency ν_2 when effecting excitation via the intermediate state $2p_6$ ($5p[\frac{3}{2}]_2$). The Rydberg states were identified and the transition frequencies for them calculated using the results reported by Delsart *et al* (1981). The arrow indicates the relative position of the green line of the copper-vapour laser.

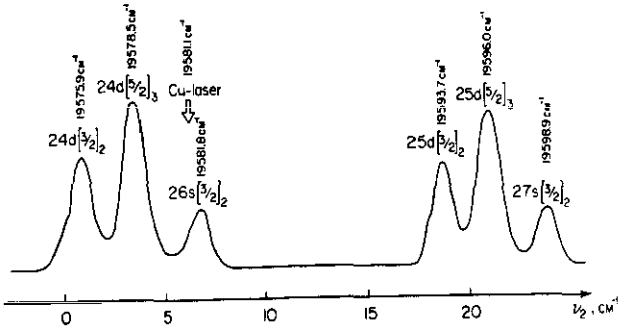

Figure 3. Photoion signal as a function of the second-step laser frequency ν_2 ($\lambda_1 = 7602$ Å). The Rydberg states were identified and the absolute transition frequency values calculated using the results of Delsart *et al* (1981). The arrow indicates the position of the green line of the copper-vapour laser.

4. Laser photoionization efficiency. Background noise signal

The Doppler frequency shift in the absorption spectrum of the accelerated atomic beam is defined by the expression $\Delta\nu \approx \pm(\nu/c)(2e(U_A - U_R)/m)^{1/2}$, where ν is the atomic transition frequency, c the velocity of light in vacuum, and m the atomic mass. By adjusting appropriately the atomic beam energy, any atomic transition to one of the neighbouring Rydberg states of figure 3 can be made to resonate with the green line of the copper-vapour laser. To excite the $24d[\frac{3}{2}]_2^o$ state, which could be accomplished at a beam energy of $e(U_A - U_R) \simeq 2.7$ keV, was technically most suitable in our experimental conditions. To this end, the green-line radiation was collimated with a telescope and entered by means of the mirror M (figure 1) to follow the accelerated atomic beam.

Figure 4 shows the photoion signal N_i as a function of the charge-exchange cell potential U_R. The potential U_+ was varied concurrently with U_R so as to make all the photoions pass through the slit S and reach the detector, no matter what the potential U_R. With the bandwidth $\Delta\nu_1$ of the first-step excitation dye laser being as wide as 1 cm^{-1}, all the isotopic Kr atoms in the beam remained in resonance with the laser radiation throughout the U_R range. As can be seen from figure 4(a), the bandwidth of the copper-vapour laser was too great for the isotopic structure of the accelerated atomic beam to be resolved.

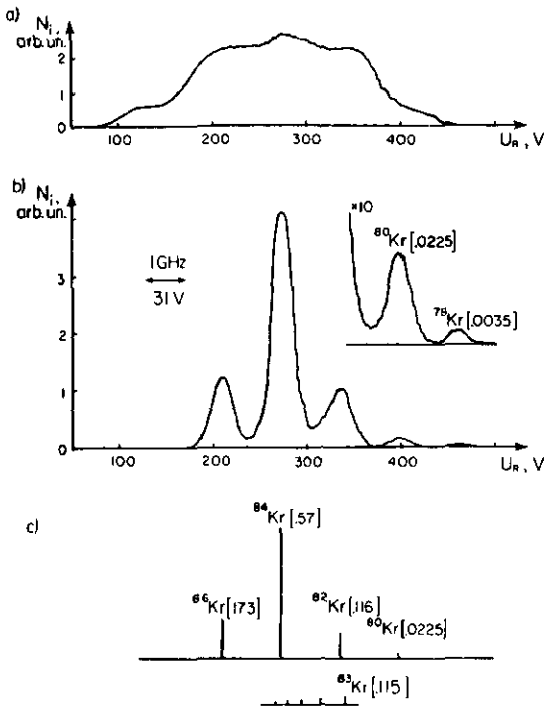

Figure 4. (a) Photoion signal as a function of the charge-exchange cell potential U_R ($U_A = 3$ kV). The $2p_6$ ($5p[\frac{3}{2}]_2$) → $24d[\frac{3}{2}]_2^o$ transition is excited using the green line of the copper-vapour laser. (b) As figure 4(a) but with the copper-vapour laser light passing additionally through two Fabry–Perot interferometers 0.5 and 0.17 cm^{-1} in free spectral range. (c) Calculated relative positions and intensities of the accelerated Kr isotope beam resonances with the narrow-band laser radiation.

With the atomic transitions at both laser excitation steps being saturated, around 4% of the accelerated Kr atoms contained in the field-free region at the moment of excitation were detected in the form of photoions.

Really, the probability that an accelerated Kr atom residing in the field-free region at the moment of excitation will be detected is $\eta = \eta_{1s_5}\eta_L\eta_D\eta_\tau(1-\eta_R)$, where η_{1s_5} is the probability that the atom will be in the $1s_5$ state after exchanging its charge, η_L is the probability of laser excitation of the atom from the $1s_5$ state to a Rydberg state, which is determined, with the atomic transitions being saturated, by the statistical weights of the active levels, η_τ is a factor depending on the radiative decay of the intermediate $2p_6$ level to states other than the initial state $1s_5$ during laser excitation, η_R is the probability that the Rydberg state will decay before the atom enters the ionizing electric field, and η_D is the probability that the photoion produced will be detected. Assuming that the quasiresonant charge exchange gives rise mainly to those states which are close to resonance, namely, $1s_2$, $1s_3$, $1s_4$ and $1s_5$, and that the populations of these states are governed by their statistical weights, the proportion of the atoms residing at the $1s_5$ level will be $\eta_{1s_5} = \frac{5}{12}$ of all the neutral atoms. When the exciting light is linearly polarized, the delay time between the first- and second-step excitation pulses is zero, and the atomic transitions are saturated, $\eta_L = \frac{1}{3}$. The lifetime of the Rydberg states in Kr is some 6 μs (Delsart *et al* 1981). In that case, $(1-\eta_R) \simeq \frac{1}{2}$. The photoion detection efficiency is $\eta_D \simeq 0.7$, and $\eta_\tau \simeq 0.9$. As a result, to register a signal from the field-free region, we have $\eta \simeq 4.4\%$, which agrees well with our measurement results.

The background noise signal due to collisions between the accelerated Kr atoms and the residual gas molecules in the system was measured with the exciting laser radiation being either shut off or away from resonance. At a system pressure of 3×10^{-7} mmHg, the background noise level γ amounted to 0.8×10^{-7} of the flow of neutral Kr atoms, I_3. Thus, the ratio between the collisional background noise and the maximum Kr photoion signal was 2×10^{-6}. Note, however, that the collisional background noise level can be brought down in a linear fashion by reducing the residual gas pressure in the vacuum system.

5. Isotope-selective photoionization

To narrow the bandwidth of the copper-vapour laser, two Fabry–Perot interferometers 0.5 and 0.17 cm^{-1} in free spectral range were set up normal to the laser beam at the entrance to the vacuum system and adjusted for maximum transmission. The distance between the interferometers and the laser was 7 m, so that reflections from the interferometer mirrors had no effect on the laser.

Figure 4(b) shows the photoion signal as a function of the charge-exchange cell potential for this case. Shown in figure 4(c) below are the calculated relative positions and intensities of the absorption lines due to the isotopic structure of the accelerated atomic beam. The distance between the absorption lines of the adjacent even Kr isotopes is 62 V, which corresponds to 2 GHz. The hyperfine structure of the odd isotope ^{83}Kr was calculated using the parameters A and B furnished by Husson *et al* (1979).

The absorption peaks of the even Kr isotopes are well resolved in the absorption spectrum of the accelerated beam (figure 4(b)). The isotope ^{78}Kr, whose relative abundance is 0.35%, can clearly be seen. The width of the peaks is governed by the

laser bandwidth $\Delta\nu_2 = 0.6$ GHz. Note that no high isotopic selectivity can be achieved when exciting rare isotope atoms with such a radiation, its bandwidth being large and contrast limited.

6. Method of detecting rare Kr isotopes

A highly selective laser excitation of rare Kr isotopes can be accomplished by using two cw single-frequency dye lasers in conjunction with pulsed dye laser amplifiers pumped by a copper-vapour laser. In that case, use can be made of the schemes for exciting Rydberg states in Kr via the intermediate level $2p_3$ (figure 2). With the laser pulse duration τ_p equal to 15 ns, the amplified radiation bandwidth will be $\Delta\nu_{1,2} \geqslant 1/2\pi\tau_p = 10$ MHz, which will allow the atomic transitions to be readily saturated.

Figure 5 presents the theoretical $1s_5 \rightarrow 2p_3$ ($\lambda_1 = 5570$ Å) absorption spectrum of Kr isotopes in an atomic beam accelerated to an energy of 10 keV. The hyperfine splitting was calculated using the parameters furnished by Husson *et al* (1979). The artificial Doppler isotope shift between the adjacent isotopes reaches 1.6 GHz, whereas the natural isotope shift on this line is around 50 MHz (Jackson 1979). With the atomic energy spread in the beam amounting to 0.5 eV, the residual Doppler width of the absorption line is $\Delta\nu_D = 11$ MHz. The natural width, 2Γ, of the absorption lines of Kr at both excitation steps depends on the lifetime of the intermediate level $2p_3$ and equals 6.1 MHz.

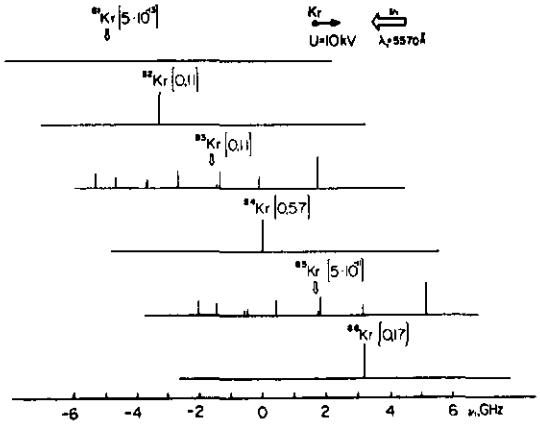

Figure 5. Theoretical relative positions of the $1s_5 \rightarrow 2p_3$ ($\lambda_1 = 5570$ Å) absorption lines of Kr isotope atoms in a beam accelerated to 10 keV. The laser light propagates counter to the atomic beam.

The extreme right hyperfine splitting component of the absorption line of the isotope ^{85}Kr, which corresponds to the $F'' = \frac{13}{2} \rightarrow F' = \frac{11}{2}$ transition, is 1.9 GHz distant from the nearest absorption line of the stable isotope ^{86}Kr. The laser excitation selectivity for ^{85}Kr is determined by absorption on the wings of the lines of all the other isotopes (mainly ^{86}Kr). The selectivity S_1 at the first excitation step is around 10^5. At the second excitation step, $5p'[\frac{1}{2}]_1$ ($F' = \frac{11}{2}$) $\rightarrow 24d[\frac{3}{2}]_2^0$ ($F = \frac{9}{2}, \frac{11}{2}, \frac{13}{2}$) (0.35 GHz distant from the ^{86}Kr line), the selectivity is $S_2 \simeq 3 \times 10^3$. For the two-step laser excitation selectivity, we then have $S \geqslant S_1 \times S_2 \simeq 3 \times 10^8$.

However, the detectivity for rare krypton isotopes will be limited by the collisional background noise and not by the laser excitation selectivity. To illustrate, with the residual gas pressure in the vacuum system ranging between 10^{-7} and 10^{-9} mmHg, the ratio between the background noise signal and the maximum photoion signal will be from 10^{-6} to 10^{-8}.

The background noise can be drastically decreased and the detection selectivity improved by means of the collinear laser photoionization of accelerated atoms in a beam obtained through charge exchange from a beam of ions at the exit of a mass separator. Let us consider the capabilities of such a technique in detecting, for example, the isotope ^{85}Kr with a relative abundance of $c = 5 \times 10^{-11}$.

Let the mass separator increase the concentration of the rare isotope in the ion beam by a factor of $\alpha = 10^5$. This means that with the total ion flow of all the Kr isotopes at the entrance to the mass separator being $N = 10^{12}\ s^{-1}$ (160 nA), the flow of ions at the exit from the separator will be $N/\alpha = 10^7\ s^{-1}$, of which 50 s^{-1} are ^{85}Kr ions. For estimation purposes, the charge-exchange coefficient k of the ion beam can be taken equal to $\frac{1}{2}$. The laser excitation efficiency for ^{85}Kr will be determined by the statistical weights of the hyperfine structure sublevels interacting with the laser light. In the case of excitation with linearly polarized light by the scheme $5s[\frac{3}{2}]^o_2$ $(F''=\frac{13}{2}) \rightarrow 5p'[\frac{1}{2}]_1$ $(F'=\frac{11}{2}) \rightarrow 24d[\frac{3}{2}]^o_2$ $(F=\frac{9}{2}, \frac{11}{2}, \frac{13}{2})$, the laser excitation efficiency η_L will be equal to $\frac{7}{50}$. Then, with $\eta_{1s_5}=\frac{5}{12}$ and $\eta_\tau(1-\eta_R)\eta_D=\frac{1}{3}$, the detection efficiency for the ^{85}Kr atoms residing in the field-free region at the moment of excitation will be

$$\eta = \eta_{1s_5}\eta_L\eta_\tau(1-\eta_R)\eta_D \simeq 0.02.$$

The ^{85}Kr ion counting rate is defined by the expression $N_i = \eta \times k \times c \times N \times \tau_d \times f$, where f is the laser pulse repetition frequency and τ_d is the detection time for the photoions coming from the field-free region. At $f = 10^4$ Hz and $\tau_d = 7\ \mu s$, we have $N_i = 3.5 \times 10^{-2}\ s^{-1}$ or 126 pulses per hour. If the residual gas pressure in the photoionization region is kept at 10^{-9} mmHg, the collisional background noise level γ will be 3×10^{-10} of the total atomic flow kN/α, and the background ion counting rate will be $N_b = \gamma(kN/\alpha)f\tau_d \simeq 10^{-4}\ s^{-1}$ or 0.36 pulses per hour.

7. Conclusion

Our experiments and estimates have shown that the suggested method should allow for reliable detection of the rare isotope ^{85}Kr ($[^{85}Kr] = 5 \times 10^{-11}$). The hyperfine splitting for the isotope ^{81}Kr ($I = \frac{7}{2}$) is unknown, but it might be expected that the same laser excitation efficiency and selectivity values can be attained for this isotope as for ^{85}Kr by properly selecting the atomic beam energy and hyperfine structure component. In that case, with the relative abundance $[^{81}Kr] = 5 \times 10^{-13}$, the photoion signal will amount to 1.2 counts per hour at a background noise level of 0.36 counts per hour. Sensitivity can be improved by increasing the atomic beam current or using specimens pre-enriched with ^{81}Kr.

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